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AN EASY COUPLING OF ACID CHLORIDES INTO α-DIKETONES PROMOTED BY DIIODOSAMARIUM

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Abstract

In THF solution at room temperature, a very fast reaction occurs between acid chlorides RCOCl and two equivalents of diiodosamarium. The α-diketone RCOCOR are obtained in yields from 40 % (R = alkyl) to 80 % (R = aryl).

We recently described reducing properties of SmI_2 and YbI_2 in THF solution[1]. SmI_2 is easily prepared from samarium metal and 1,2-diiodoethane and can be stored for a long time in THF solution under an inert atmosphere. We report here our preliminary results showing an unexpected behaviour of acid chlorides. When adding at room temperature an acid chloride RCOCl to two equivalents of SmI_2 in THF solution, a reaction very quickly occurs, as indicated by the fast disappearance of the characteristic blue-green color of SmI_2. The main product is the α-diketone RCOCOR, the α-ketol RCOCHOHR being generally one of the by-products. Some representative results are indicated in Table 1. Yields reported in this Table are those of isolated products obtained under standard conditions. As in other experiments mediated by SmI_2[1], yields of α-diketones can be probably improved by minor modifications of the reaction procedure.

The following procedure is typical : 2.5 mmoles of benzoylchloride in a few ml of THF are slowly added under nitrogen at room temperature to 5 mmoles of a 0.1 M SmI_2-THF solution. This solution turns yellow in a few minutes. Dilute HCl is then added. After ether extraction, washing by aqueous $NaHCO_3$ and drying on magnesium sulfate, 1.87 mmoles of benzil (mp = 92-94°C) is recovered after recrystallization (yield = 78 %).

One can find many examples of reducing agents opposed to acid chlorides. The most frequent reaction is the reduction into an aldehyde. The use of zerovalent complexes of nickel or enneacarbonyl diiron leads to the formation of symmetrical ketones R-CO-R[6]. Acyloin reactions for carboxylic acid chlorides were not very developped[7]. Low-valent titanium species transformed benzoyl chloride into tetraphenylfuran in high yield, presumably through an initial coupling into benzil[8]. A closer precedent to our reaction can be found in the action of beryllium metal powder on RCOCl[9]. Yields in α-diketone are 40-50 %. Tentatively the reaction is presumed to involve the organometallic species RCO-BeX[9].

The mechanism of the samarium-mediated reaction on acyl chlorides has not been investigated. According to our previous reports[1,2], the reaction presumably starts by an electron transfer from SmI_2 to RCOCl. The radical anion $(RCOCl)^{\bullet -}$ thus formed should be cleaved into $RCO^{\bullet}$ and Cl^{-}. At this stage, the radical $RCO^{\bullet}$ has two options open to it : it can dimerize into α-diketone[10] or it can be reduced into an acyl anion species[12]. The diketone is then obtained by the acylation of this species. Preferential formation of α-ketol from t-BuCOCl could result of a subsequent reduction by SmI_2 or by direct dimerization of the acyl anion $tBuCO^-$ considered as a carbene in a limiting resonance structure (see in ref.13 for a discussion of another case). To better describe this mechanism additional experiments will be necessary. We are also looking for extending the scope of this reaction, especially to prepare cyclic α-diketones or dissymmetric α-diketones.

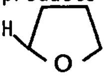
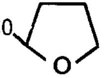
TABLE 1

Acid chloride	Reaction time[a]	Products (Yields)[b]	
Ph-COCl[c]	2 min.	Ph-CO-CO-Ph	(78 %)
p-OMeC_6H_4-COCl[c]	6 min.	p-OMeC_6H_4-CO-CO-(p-OMeC_6H_4)	(69 %)
p-ClC_6H_4-COCl[c]	4 min.	p-ClC_6H_4-CO-CO-(p-ClC_6H_4)	(72 %)
n-C_8H_{17}-COCl[d]	10 min.	n-C_8H_{17}-CO-CO-(n-C_8H_{17})	(50 %)[e]
t-Bu-COCl[d]	20 min.	t-Bu-COCHOH-(t-Bu)	(46 %)
Cl-$(CH_2)_4$-COCl[d]	8 min.	$Cl(CH_2)_4$-CO-CO-$(CH_2)_4Cl$	(54 %)

[a] The end-point of the reaction is indicated by the disappearance of the blue-green color of SmI_2.

[b] Yields in isolated products purified either by column chromatography or by recrystallization

[c] 2.5 mmol RCOCl and 5 mmol SmI_2. [d] 5 mmol RCOCl and 10 mmol SmI_2.

[e] Two other products were isolated. They are "solvent addition" compounds presumably nC_8H_{17}-CHOH  (18 %) and nC_8H_{17}-CO  (14 %).

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(3) Several methods have been described for the preparation of α-diketones[4] and are mostly limited to the oxidation of acyloins, acetylenic compounds or diols. α-diketones were also prepared from aldehydes and alkyl iodides using $Fe(CO)_5$ as carbonylating agent[5].

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(12) Nucleophilic acylation is a useful method for organic synthesis[13,14]. However few acylmetal compounds are known,the method proceeds mainly by "masked" acyl anions.The hypothetical intermediate depicted in ref.9 should be considered as an acyl anion of beryllium.

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